FROM IRON ORE TO ECOTOXIOLOGICAL IMPACTS: ONE THOUSAND YEARS OF MANGANESE HISTORY.

Quentin Petitjean [(1)], A-V. Walter-Simonnet [(1)], F. Choulet [(1)], Anne-Lise Mariet [(1)], P. Goncalves [(1)], H. Laurent [(2)], P. Rosenthal [(1)], A. de Vaufleury [(1)], F. Gimbert [(1)].

[(1)] ***UMR 6249 Chrono-Environnement, CNRS-Université de Bourgogne Franche-Comté, 16 route de Gray, 25030 Besançon Cedex.***
[(2)] ***DRAC Bourgogne-Franche-Comté - site de Besançon 7 rue Charles Nodier, 25043 Besançon Cedex.***
frederic.gimbert@univ-fcomte.fr

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Introduction

In human history, socio-economic development was strongly influenced by metal resources through mining and metallurgical activities, for instance, of lead (Pb), silver (Ag), or iron (Fe) (Tylecote, 1987). However, they can lead to a significant environmental contamination through the emission of metal-rich particles and wastes. Hence, Mariet et al. (2016) recently showed that heavy metal (HM) from mining operations (Pb and Ag) in the Vosges mountains (France) at the end of Middle Ages are still bioavailable to soil invertebrates. In the region Franche-Comté, iron mining and metallurgical activities were dominant over the Middle-Age period, especially in the ancient iron production district of Berthelange (Forlin and Laurent, 2014). However, according to our knowledges, the environmental impacts have not been evaluated. Therefore, this study aims at assessing the fate of heavy metals from very ancient (1000 years) slag heaps in soil using combined physical, chemical and biological approaches.

Methods

The target area which is a slag repository from the XI^{e} century (direct ore reducing process) was sampled by a transect method (from the center of the heap, n=10). A characterization of soil samples and slags was performed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to determine the mineralogical content of the iron ore, slags and their weathering products in soils. Secondly, the HM total concentrations and available (exchangeable and reducible) fractions were determined (ICP-AES) in soils after *aqua-regia* digestion and ammonium acetate (NH_4OAc, 1M) + 2% hydroxylamine hydrochloride (NH_2OH, HCl) extraction, respectively. Finally, we carried out a bioaccumulation and toxicity bioassay (growth inhibition, ISO 15952) using the land snail *Cantareus aspersus* exposed to contrasted contaminated soils from the site.

Results

Soil analyses revealed slight anomalies for arsenic (As), copper (Cu) and zinc (Zn), about twice the enquiry threshold set by Baize (2000). On the other hand, manganese (Mn) held very high concentrations in soil, for instance reaching about 8000 mg.kg^{-1} (dry weight) at the center of the slag heap (SP4, Figure 1). Iron ore, mainly composed of hematite and goethite, contained 330 mg.kg^{-1} while slags reached about 17,000 mg.kg^{-1} of Mn. This elevated concentration reached in slags may be related to the smeltering process that led to the synthesis of olivine (Mn-fayalite – $(Mn,Fe)_2SiO_4$). The soil mineralogical analyses allowed to identify the presence of serpentine which is an evidence of olivine weathering. This degradation of slags led to the release of their HM and particularly Mn in the soil. A large part of this Mn appeared available, at least for partitioning with the soil solution and transferring to organisms (plants or invertebrates). Although no growth inhibition of snail was observed after 28 days of exposure, the animals were able to accumulate quite elevated Mn concentrations in their tissues.

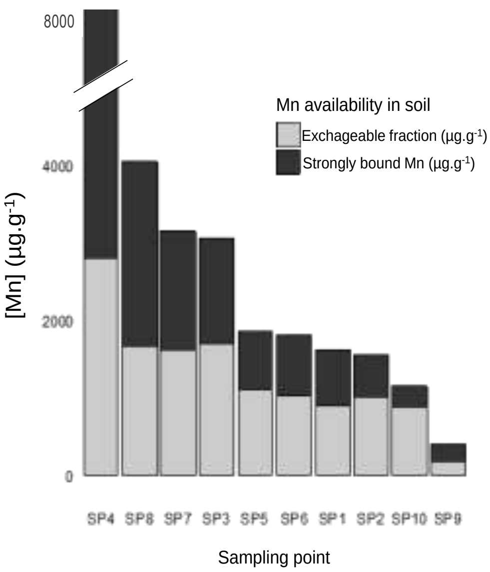

Figure 1. Total Mn concentrations in soils (*aqua regia*, grey + black) and Mn environmental availability (ammonium acetate, grey).

Conclusion

The combination of various approaches clearly emphasized the environmental availability and bioavailability of HM from ancient metallurgical wastes to soil-dwelling invertebrates such as snails even one millennium after their deposit. For these reasons, past mining ecosystems must be, as is the case for more recent industrial sites, a cause of concern for both the scientific community and the public authorities.

References

Baize D. (2000). Teneurs totales en “métaux lourds” dans les sols français. Résultats généraux du programme ASPITET. *Cour. Environ. INRA* 39, 39-54.

Forlin, P., Laurent, H. (2014). Exploiting local resources in a new economic frame: Iron ores and bloomeries in Franche-Comté during the Early Middle Ages. IES Yearbook, 196 – 217.

ISO 15952 (2006). Soil quality—effects of pollutants on juvenile land snails (Helicidae)—determination of the effects on growth by soil contamination, International Organization for Standardization, Geneva, Switzerland.

Mariet A., de Vaufleury A., Bégeot C., Walter-Simonnet A.V., Gimbert F. (2016). Palaeo-pollution from mining activities in the Vosges Mountains: 1000 years and still bioavailable. *Environ. Pollut.*, in press.

Tylecote, R.F. (1987). The Early History of Metallurgy in Europe. Ed. Longman, London and New York.

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